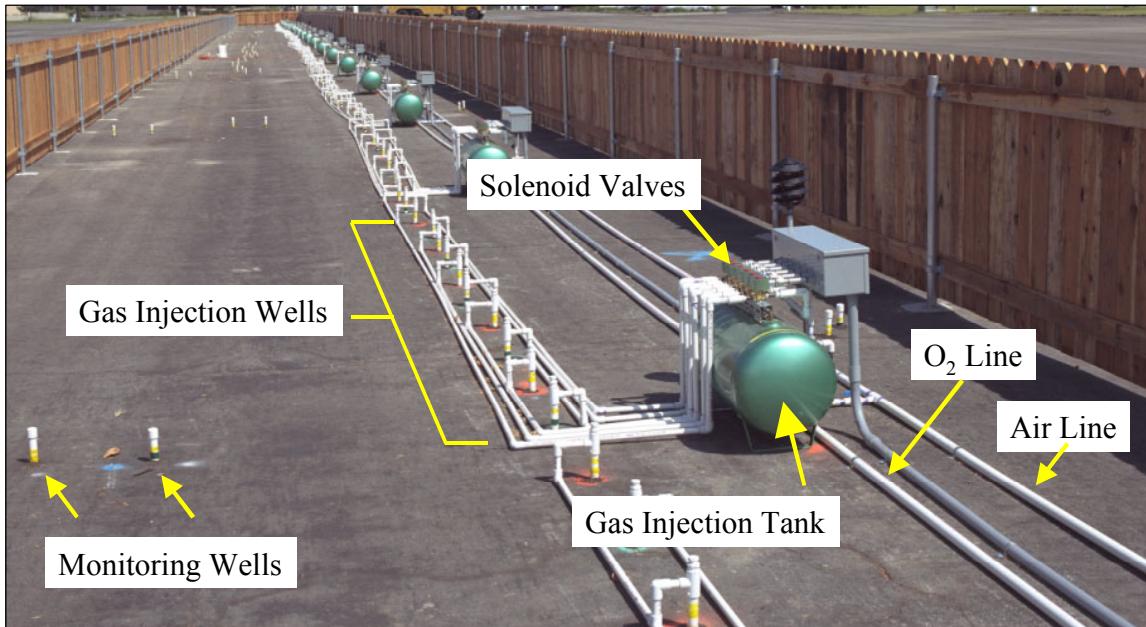


TECHNICAL REPORT TR-2257-ENV

A PRACTICAL APPROACH TO THE DESIGN, MONITORING, AND OPTIMIZATION OF IN SITU MTBE AEROBIC BIOBARRIERS



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EXECUTIVE SUMMARY

This document presents a paradigm for the design, monitoring, and optimization of in situ methyl tert-butyl ether (MTBE) aerobic biobarriers. In this technology, an oxygen-rich biologically reactive treatment zone (the “biobarrier”) is established in situ and down-gradient of the source of dissolved MTBE contamination in groundwater (typically gasoline-impacted soils resulting from leaks and spills at service station sites or other fuel storage and distribution facilities). The system is designed so that groundwater containing dissolved MTBE flows to, and through, the biobarrier treatment zone (ideally under natural gradient conditions so that no pumping is necessary). As the groundwater passes through the biobarrier, the MTBE is converted by microorganisms to innocuous by-products (carbon dioxide and water). Ideally, the groundwater leaving the down gradient edge of the treatment zone contains MTBE at concentrations less than or equal to the treatment target levels. The system also reduces concentrations of other aerobically degradable chemicals dissolved in the groundwater (e.g., benzene, toluene, xylenes, and tert-butyl alcohol).

The technology discussed in this document is applied for the purposes of containing or preventing further migration of existing dissolved MTBE groundwater plumes, or for the purpose of eliminating future MTBE discharge to an aquifer at the down-gradient edge of an MTBE source zone. This technology is not a source zone treatment remedy. At some sites, this technology will be more cost-effective than conventional groundwater extraction and above-ground treatment “pump and treat” systems. Relative to pump and treat systems, this technology will be most economically attractive at shallower and less hydrologically-complex sites where the installation of a high density of wells is not cost-prohibitive, and where oxygen is easily delivered to the target treatment zones.

This design paradigm is based on experience gained while designing, monitoring, and optimizing pilot-scale and full-scale MTBE biobarrier systems – most notably, the systems studied at the Naval Base Ventura County (NBVC) at Port Hueneme, CA. It is largely empirically-based, although the design approach does rely on simple engineering calculations. In addition, the document emphasizes gas injection-based oxygen delivery schemes, although it is acknowledged that there are other methods for delivering oxygen to aquifers. Full-scale performance data for a system designed using this approach and cost estimation tools are found in Miller et al. (2003a) and Miller et al. (2003b), respectively.

ABBREVIATIONS AND ACRONYMS

ASU	Arizona State University
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
DO	dissolved oxygen
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
MTBE	methyl-tert-butyl ether
NFESC	Naval Facilities Engineering Service Center
NBVC	Naval Base Ventura County
TBA	tert-butyl alcohol

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CHAPTER 1. INTRODUCTION

1.1 BACKGROUND

Methyl tert-butyl ether (MTBE) is a fuel oxygenate that is often found in groundwater beneath sites that store and distribute petroleum fuels. This chemical has been added to gasoline since the late 1970's. Initially it was added at concentrations of about 2% by volume for octane enhancement, and more recently it is being blended at concentrations of up to 15% by volume to meet today's cleaner burning fuel requirements.

Its frequent occurrence in groundwater beneath fuel distribution sites is reflective of its chemical properties; it has a relatively high water solubility, a relatively low organic carbon sorption coefficient, a relatively low Henry's Law Constant, and is more slowly degradable in comparison with other fuel chemicals of concern (e.g., benzene, toluene, ethylbenzene, xylenes - BTEX). There is evidence that MTBE may migrate farther and faster in groundwater, and persist longer than other fuel components of concern at some sites. For example, the MTBE plume emanating from the Naval Base Ventura County (NBVC), Port Hueneme service station is now over 150 m (500 ft) wide and over 1500 m (5000 ft) long. It outdistances the dissolved BTEX plume by over 4,000 feet. Other studies suggest that dissolved plumes of this length are not typical; for example, Happel et al. (1998), Mace and Choi (1998), Reid et al. (1999), and Wilson et al. (2001) concluded that many MTBE plumes appear to not be much longer than their associated dissolved benzene plumes at this time. Nevertheless, a number of longer plumes have been identified (Vandenberg, AFB; Novato, CA; East Patchogue, NY) and there are already a number of well-publicized municipal well-impacts (Santa Monica, CA; Lake Tahoe, CA; Marysville, CA; and Glennville, CA).

In cases where the dissolved MTBE plumes are not attenuated sufficiently by natural processes, there may be a need to contain the expansion of the dissolved plumes and to prevent further discharges to the aquifers at the source zones. Historically, containment has been accomplished hydraulically through groundwater extraction followed by above-ground treatment and discharge (more commonly referred to as "pump and treat"). More recently, it has been shown (Salanitro et al. 2000 and Wilson et al. 2002) that dissolved MTBE plumes might be contained by employing in situ flow-through "biobarriers". These systems are attractive because they rely on natural groundwater flow, they do not require maintenance-intensive groundwater extraction, above-ground treatment, and discharge systems, and at some sites will be more cost-effective than conventional pump and treat systems.

This document proposes a design paradigm for the design, operation, monitoring, and maintenance of aerobic MTBE biobarrier systems based on lessons learned to date from pilot test and demonstration studies conducted by the authors.

1.2 TECHNOLOGY OVERVIEW

As depicted in Figure 1, an oxygen-rich biologically reactive treatment zone (the “biobarrier”) is established in situ and down-gradient of the source of dissolved MTBE contamination (typically gasoline-impacted soils resulting from leaks and spills at service station sites or other fuel storage and distribution facilities). The system is designed so that groundwater containing dissolved MTBE flows to, and through, the biobarrier treatment zone. The use of natural flow conditions is preferred, but one can imagine groundwater pumping schemes that direct impacted groundwater to a treatment zone. As the groundwater passes through the biobarrier, the MTBE is converted by microorganisms to innocuous by-products (carbon dioxide and water). Ideally, groundwater leaving the down-gradient edge of the treatment zone contains MTBE at concentrations less than or equal to the target treatment levels. A system designed to treat MTBE will also very likely reduce concentrations of other aerobically biodegradable chemicals dissolved in the groundwater (e.g., benzene, toluene, xylenes, and tert-butyl alcohol).

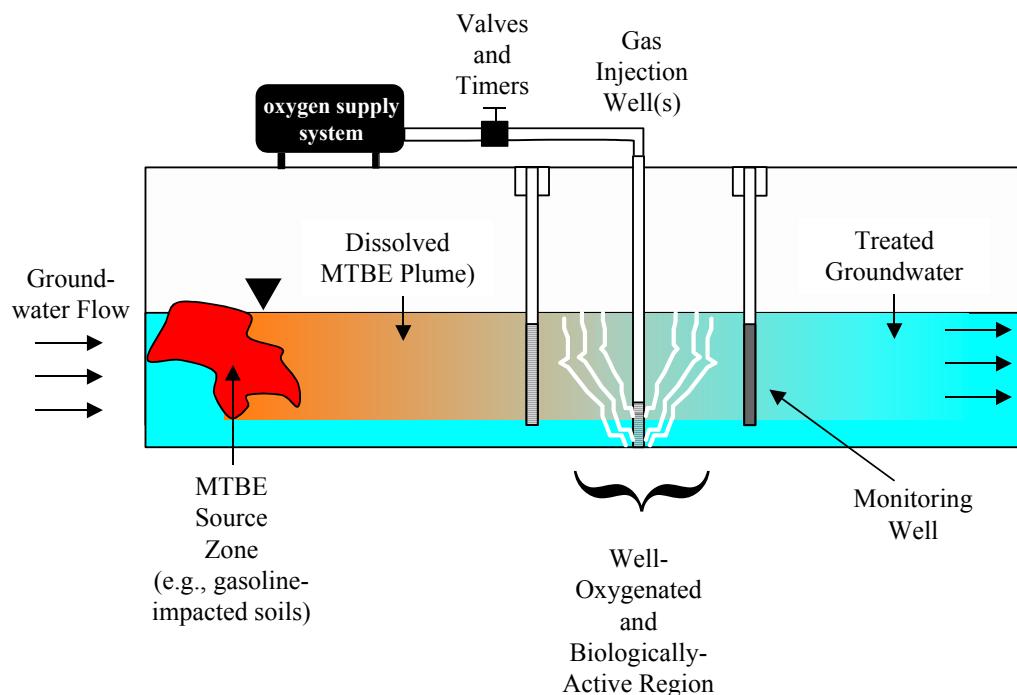


Figure 1. Simplistic schematic of an aerobic MTBE biobarrier system operated under natural flow conditions.

In Figure 1, oxygenation of the aquifer is accomplished through periodic oxygen (or air) injection via a line of gas injection wells spanning the width of the dissolved MTBE plume. In this approach, gas injection is of high intensity (e.g., gas flows of $>0.3 \text{ m}^3/\text{min} = 10 \text{ ft}^3/\text{min}$ for durations of about a minute) and periodic (e.g., daily) to achieve sufficient gas distribution while not altering the natural groundwater flow through the treatment zone. While there are a number of ways to deliver oxygen to groundwater (e.g., in-well oxygenation systems and oxygen-releasing compounds), this document focuses on gas injection because that is the approach that was successfully demonstrated at full-scale (Miller et al., 2003a, b).

Other than the up- and down-gradient groundwater monitoring wells, the only process components required for this technology are associated with the oxygen delivery system. For the gas injection approach illustrated in Figure 1, these might typically include an oxygen generator (or air compressor), oxygen or air storage tanks, gas injection wells, and a series of timers and solenoids to control and direct the oxygen to the gas injection wells.

In some cases, oxygen addition will stimulate the growth of indigenous MTBE-degrading organisms, and the growth rate and activity of these organisms will be sufficient to effect the desired reduction in concentration. At other sites, the microbial community may not contain the necessary organisms, or the growth rate and activity may be too low to achieve the desired concentration reduction within an acceptable time frame. In those cases it may be necessary to inoculate the aquifer with MTBE-degrading cultures.

1.3 TECHNOLOGY DEVELOPMENT AND DEMONSTRATION HISTORY

This technology has been in development for over a decade. In the early 1990's Shell Development (now Shell Global Solutions) researchers identified and enriched a mixed culture (MC-100) capable of completely degrading MTBE to carbon dioxide and water (Salanitro 1994). In the mid- to late-1990's MTBE degradation was demonstrated in flow-through column experiments conducted using sand columns inoculated with MC-100. In the late 1990's, a single MTBE-degrading organism (SC-100) was isolated from the mixed culture.

The bench-scale studies and ability to produce the MTBE-degrading cultures at a large enough scale led to pilot-scale studies conducted collaboratively between Shell Global Solutions (then Equilon Enterprises, LLC), Arizona State University (ASU), and the Naval Facilities Engineering Service Center (NFESC). Six pilot-test plots were eventually installed at the Naval Base Ventura County (NBVC) at Port Hueneme, CA. The plots examined the performance of 20-ft wide biobarriers employing various combinations of oxygen and air injection and the mixed- and single-cultures MC-100 and SC-100. All were placed far down-gradient of the source zone where groundwater contained only MTBE and TBA. In brief, the pilot-tests confirmed that the aquifer could be successfully bioaugmented with no loss of biobarrier activity over time. Concentrations of MTBE were reduced from roughly 700 - 2000 ug/L to non-detect concentrations (<5 ug/L MTBE) and TBA was also reduced to non-detect levels (<50 ug/L TBA). These studies demonstrated that the overall activity of naturally-occurring MTBE-degraders could be stimulated by increasing the dissolved oxygen levels in groundwater; the activity in the biostimulated plot became comparable to the bioaugmented plot after about 240 d of operation. The short-term performance of MC-100 bioaugmented and the biostimulated test plots are reported in Salanitro et al. (2000).

The success of these pilot tests led to the ESTCP-sponsored full-scale demonstration at NBVC. This system, pictured below in Figure 2, spanned the approximately 500-ft wide dissolved MTBE plume and it was constructed immediately down-gradient of the source zone at that site. This system was operated and monitored for approximately 18 months, and the cost and performance data are discussed in Miller et al. (2003a, b). In brief, the system was comprised of sections involving air injection only, oxygen injection only, and oxygen injection plus

bioaugmentation with either the MC-100 or SC-100 cultures. Air injection occurred in the lower concentration (<100 ug/L) plume fringes, while oxygen gas addition and bioaugmentation sections were aligned with the central core of the plume where combined concentrations of MTBE, TBA, and BTEX components were in excess of 10,000 ug/L. This full-scale system effected concentration reductions to non-detect levels (<5 – 10 u/L) for all chemicals studied.



Figure 2. Full-scale biobarrier located at NBVC, Port Hueneme, California (groundwater flows from right to left).

1.4 LESSONS LEARNED TO DATE

Based on the pilot-scale and field-scale applications to date, the following are key lessons-learned that are particularly relevant to the design paradigm discussed below:

Source Zone Delineation: At most sites, the down-gradient edge of the source zone is not well-delineated and practitioners should plan for additional characterization to insure that the biobarrier is placed down-gradient of all MTBE sources.

Oxygen Delivery via Gas Injection: Oxygen delivery via pulsed high-intensity gas flow can be effective at increasing DO levels while not altering the natural groundwater flow rate and direction. In addition, there are two benefits of this method: a) trapped gas left in the aquifer

pores between injections can be a continuing source of oxygen for days to weeks, thus allowing time to handle unexpected system shut-downs without compromising system performance, and b) oxygen is delivered throughout the whole treatment zone rather than at one up-gradient location (as is the case for in-well oxygen addition schemes).

Dissolved Oxygen (DO) Levels: Field tests have demonstrated that elevated DO levels (as high as 30 – 40 mg/L) are not detrimental to the MTBE- and hydrocarbon-degrading organisms. Pilot-scale tests also suggest that there may be advantages to using oxygen gas injection instead of air injection; in particular, the higher equilibrium DO level (approx. 40 mg/L for O₂ gas vs 8 mg/L for air) may off-set the spatially non-uniform nature of gas distributions in aquifers.

Biostimulation: If the native microbial population contains the necessary degraders, it is likely that increased biodegradation activity will occur as a result of increasing the DO levels in the aquifer (presumably through growth of the necessary degraders). This increase in activity may, or may not be sufficient to achieve the desired concentration reductions. If it occurs, the success of biostimulation (e.g., as measured by reduced MTBE concentrations) might not be evident for six to 12 months. Microcosm tests can be used to determine the presence of aerobic MTBE-degrading bacteria in aquifer materials and groundwater; however, it is not clear how to determine *a priori* if biostimulation will result in sufficient MTBE-degrading activity. The microcosm tests themselves might require four to twelve months to definitively determine the presence of the MTBE degraders.

Bioaugmentation: MC-100 and SC-100 cultures were injected into the NBVC aquifer at high concentrations (approx. 2 mg/L total suspended solids (TSS)); the effect of this injection on MTBE concentrations was generally observed within one to three months, with no apparent loss of activity over the periods of time studied (two to three years).

Presence of Other Chemicals: The presence of other aerobically degradable fuel-related chemicals (e.g., BTEX) did not adversely affect the system performance. MTBE was degraded as effectively in the full-scale demonstration system that treated a mixed MTBE/BTEX/TBA plume as it was in the pilot test systems that treated an MTBE/TBA-only plume. In addition, the aerobic MTBE biobarrier can also be effective at reducing concentrations of the other fuel-related chemicals of concern.

CHAPTER 2. DESIGN PARADIGM

2.1 BASIC DESIGN PRINCIPLES

The following basic design principles should guide the design, operation, and monitoring of aerobic MTBE biobarrier systems:

Location: The system must be placed down-gradient of any MTBE sources (e.g., soils containing immiscible residual gasoline) and must span the full width of the dissolved MTBE

plume. Thus, delineation of the down-gradient extent of MTBE source zones and the width of the dissolved plume is critical. Otherwise, treated groundwater leaving the biobarrier will become re-contaminated when it contacts impacted soils.

Natural Environment: In its natural state, the aquifer environment must be suitable for microbial growth; for example, the pH must not be too high ($\text{pH} > 8$) nor too low ($\text{pH} < 6$) and other chemicals in the soil and groundwater should not be inhibitive of microbial growth.

Dissolved Oxygen: Concentration reductions are achieved through aerobic biodegradation; thus, the design of the oxygen delivery system is critical. The oxygen delivery system must be capable of consistently maintaining elevated dissolved oxygen (DO) groundwater levels ($> 2 \text{ mg/L}$ and preferably $> 4 \text{ mg/L DO}$) throughout the target treatment zone. Unless the total concentration of aerobically degradable chemicals is $< 1 \text{ mg/L}$, it is unlikely that a one-time up-gradient DO increase would achieve the desired effect; thus, it is important to consider systems that deliver oxygen to groundwater for about 3 – 6 m (10 – 20 ft) along the flow-path, rather than systems that deliver oxygen at only one location along the flow-path.

Groundwater Flow: MTBE-impacted groundwater must flow through the in situ treatment zone. Preferably this occurs under natural gradient conditions, although it in some cases flow direction and rate might be controlled by groundwater extraction down-gradient of the treatment zone. Effects of oxygen delivery schemes on groundwater flow-paths need to be considered.

Biostimulation vs. Bioaugmentation: For biostimulation to be an option, the indigenous bacteria population must be capable of converting MTBE to CO_2 and H_2O (and not stop at the production of the intermediate TBA). This is best demonstrated through microcosm studies using samples of aquifer material and groundwater from the site. Given the relatively slow growth rates on MTBE and low cell yields typical of MTBE-degrading bacteria (e.g., Salanitro et al., 1994), it may be necessary to conduct these studies for 4 – 12 months to see evidence of complete MTBE biodegradation.

Molecular tools offer the potential to more quickly identify the presence of specific bacterial strains known to degrade MTBE (Hristova et al., 2003). These tools can also be used to assess degrader cell densities in soils and groundwater. To be useful on a routine basis, however, these tools still need to be developed for all strains of MTBE-degrading organisms.

Demonstrating the presence of indigenous MTBE degraders with microcosm studies is not sufficient to insure the success of biostimulation; the native microbial population's degrading activity must also increase to a level that is sufficient to achieve the desired concentration reduction. At this point in time it is not clear how to determine if this will be the case on a site-specific basis except through trial and error in the field.

One option is to install the oxygen delivery system and see how the native microbial population responds to the increased DO levels. Based on the limited experience to date, one might need to wait up to 12 months to determine if there is a response. If not, or if constraints do not allow a 12 month observation period, then the inoculation (bioaugmentation) with an MTBE-degrading culture in the target treatment zone will be necessary. If that is the case, the aquifer inoculation

should only occur after the oxygen delivery system has been installed, operated, and monitored to insure that it has achieved and can maintain the target DO levels.

Time Scales: Based on experience, the effect of oxygen addition on DO concentrations in the target treatment zone are generally observed over a few weeks to a few months. Corresponding increases in biodegradation activity and concentration reductions in the target treatment zone might not be observed for a few months, but are generally observed with 6 – 12 months (if there is MTBE biodegradation occurring). MTBE degraders are generally regarded to be slow-growing low-yield bacteria, so slow response times in some settings are to be expected (as mentioned above, an eight-month period was necessary to achieve significant activity in the biostimulated biobarrier pilot-test plots at NBVC).

2.2 BASIC DESIGN PARADIGM

The sequence of steps and decisions associated with this design paradigm are presented in Figure 3 and are also discussed briefly below. More specific details associated with the design of the oxygen delivery system are discussed in §2.3.

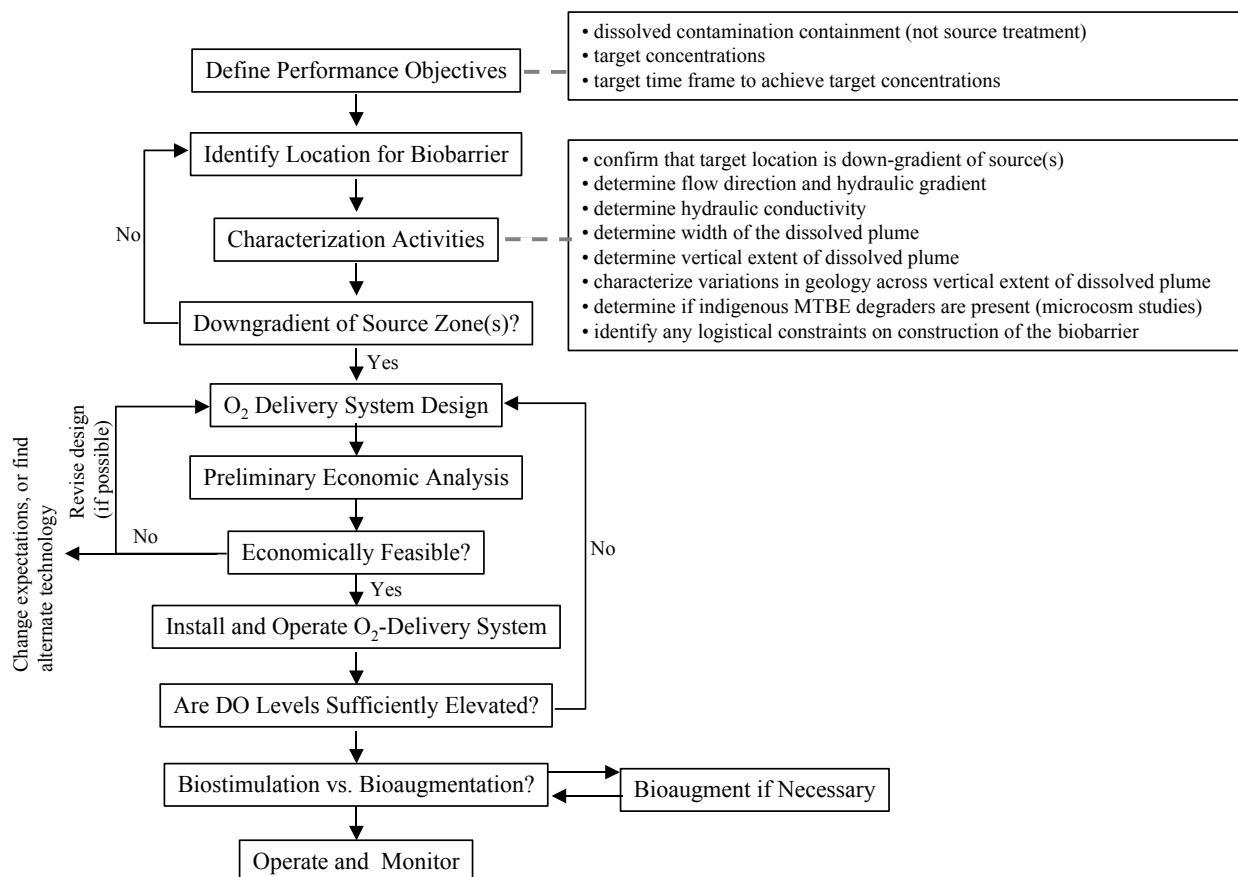


Figure 3. Design paradigm for aerobic biobarrier systems.

Step 1 - Define Performance Objectives: First, it is important to ensure that it is understood by all that this is a containment technology and not a source zone treatment remedy. Second, target dissolved MTBE concentrations immediately down-gradient of the biobarrier and the time frame required to achieve them should be specified at the beginning of the design process.

Step 2 - Identify the Location for the Biobarrier: After considering the location of the source zone, the dissolved plume boundaries, remedial objectives, and logistical issues (e.g., above-ground physical constraints and underground utilities), a preliminary location for the biobarrier is selected. The biobarrier may be placed at the leading edge of the dissolved plume to prevent further plume expansion, or it may be placed at the down-gradient edge of the source zone to prevent future MTBE migration away from the source zone (as was the case for the NBVC large-scale demonstration system). At other sites it may be placed at some intermediate location (e.g., a property boundary) to prevent migration beyond that location.

Step 3 - Characterization Activities: In addition to routine site characterization activities, activities specific to biobarrier design include the following:

- a) *Soil sampling and chemical analysis of soils* in the vicinity of the proposed biobarrier location to verify that the biobarrier is being placed down-gradient of the source zone(s). This is especially critical at sites where the biobarrier is to be placed immediately down-gradient of the source zone, as there is often uncertainty in the location of the source zone boundary after a typical site assessment. For petroleum fuel spill sites, staining and/or petroleum odors in a soil core sample is generally indicative that the core was located within the source zone. For most petroleum fuel spill sites, where the fuel is less dense than water and the spill is large enough that gasoline liquid reaches the water table, soil sampling should generally focus on the vertical interval spanning the range of historic high and low water table elevations since the release. If impacted soils are found, then a new down-gradient biobarrier location will need to be selected. Confirmation soil sampling is less critical for sites where the biobarrier is to be placed at the leading edge of the dissolved plume.
- b) *Groundwater sampling* in the vicinity of the proposed biobarrier location to define the lateral boundaries (plume width) and the vertical extent of the dissolved plume. Groundwater sampling should also identify the maximum concentrations to be treated by the biobarrier, and the spatial variability in concentrations across the width of the dissolved plume.
- c) *Soil coring* in the vicinity of the proposed biobarrier location to qualitatively assess vertical and lateral variations in geology and groundwater flow properties. At least one continuous core should be collected across the MTBE-impacted vertical interval of the aquifer to help guide the design of the oxygen delivery system.
- d) *Microcosm studies* using aquifer solids and groundwater collected during characterization activities (a) through (c) in the vicinity of the proposed biobarrier. Roughly 100 g of soil and 100 mL of groundwater is needed for each microcosm; ideally a series of

microcosms using soils from different depths and locations would be conducted, including one or more controls.

- e) *Measurement of groundwater elevations* to determine groundwater flow direction. Existing groundwater monitoring wells can be used; otherwise, the installation of groundwater monitoring wells will be necessary. If new wells are to be installed, thought should be given to maximizing the spacing of the new wells to minimize flow direction determination error resulting from the inherent inaccuracies of conventional water level measurement techniques. For example, the maximum measurable elevation difference between two wells located 30 m (100 ft) apart is 0.09 m (0.3 ft) at a site with a gradient of 0.003 m/m, while measurement errors for manual gauging using an interface probe are likely to be in the 0.015 – 0.03 m (0.05 – 0.1 ft) range. Thus, even a 30 m (100 ft) separation between three wells might lead to significant inaccuracies in the flow direction determination at sites with relatively flat hydraulic gradients.
- f) *Aquifer characterization tests* to determine the hydraulic conductivity of the aquifer and any significant vertical variations across the target treatment zone. Existing conventional groundwater monitoring wells can be used, but if possible, depth-specific determination is desirable. Core(s) collected during characterization activity (c) can also be used qualitatively assess expected variations in hydraulic conductivity, and laboratory permeability tests can be conducted on samples from the core(s).
- g) *Gas injection zone of influence characterization* (for gas injection-based oxygen delivery systems) to determine appropriate gas injection well locations and screened interval(s). The characterization/pilot test activities discussed in P.C. Johnson et al. (2001a, b), R.L. Johnson et al. (2001a, b, c) and Bruce et al. (2001) can be used for this purpose.

Step 4 – Decision: - Is the Proposed Biobarrier Location Down-gradient of the Source Zone(s)? If the data from Step 3 suggest that the answer is “no”, then the location will need to be moved down-gradient of the proposed location and Step 3 will need to be repeated. If the data suggest that the answer is “yes”, then the practitioner proceeds to Step 5.

Step 5 – Design of the Oxygen Delivery System. Prior to selecting a specific oxygen delivery process and designing the oxygen delivery system, it is useful to define the minimum performance requirements:

- a) The oxygen delivery system should not cause MTBE-impacted groundwater to flow around or beneath the target treatment zone. For the gas injection-based oxygen delivery schemes discussed here, this is accomplished by periodic (rather than continuous) gas injection.
- b) The oxygen delivery system must be capable of maintaining elevated DO concentrations (>2 mg/L DO and preferably >4 mg/L) along the length of the flow path where the biodegradation occurs.

c) With respect to (b), the system must be capable of supplying oxygen to the groundwater at a rate in excess of the following amount:

$$O_D = < q C_A > W H S \times \frac{1 m^3}{1000 L} \quad (1)$$

Where O_D is the minimum oxygen delivery rate [mg-O₂/d], $< q C_A >$ is the product of the groundwater specific discharge q [m/d] and the total concentration of aerobically biodegradable chemicals in groundwater C_A [mg/L] spatially integrated over the vertical plane defined by the plume width W [m] and plume thickness H [m] ($< q C_A > W H$) represents the total mass discharge of aerobically biodegradable chemicals in groundwater). S is the stoichiometric coefficient [mg-O₂ required/mg-chemical degraded]. Typical values of S are approximately 3 mg-O₂ required/mg-chemical degraded for hydrocarbon chemicals in groundwater at fuel spill sites.

d) Ideally, the oxygen delivery system would be robust enough that oxygen delivery would continue for several days in the vent that the above-ground (or in-well) equipment were to fail or require routine maintenance. This is a natural feature of gas delivery systems as they create pockets, or reservoirs, of trapped gas in the aquifer, and the trapped gas can continue to dissolve for days - weeks even when gas is not being injected. A rough estimate of this trapped gas oxygen reservoir capacity O_R [mg-O₂] can be calculated:

$$O_R = W H L \times 0.3 \frac{m^3 - \text{pores}}{m^3 - \text{aquifer}} \times 0.05 \frac{m^3 - \text{gas}}{m^3 - \text{pores}} \times F_O \frac{m^3 - O_2}{m^3 - \text{gas}} \times 1300 \frac{\text{mg} - O_2}{m^3 - O_2} \quad (2)$$

where F_O is the volume fraction of oxygen in the gas being injected, L is the length of the oxygenated zone [m], and it has been assumed that the volume-averaged trapped gas saturation is about 0.05 m³-gas/m³-pores.

The duration of dissolution of the trapped gas ΔT_O [d] can be approximated by:

$$\Delta T_O = \frac{L \times 0.3 \frac{m^3 - \text{pores}}{m^3 - \text{aquifer}} \times 0.05 \frac{m^3 - \text{gas}}{m^3 - \text{pores}}}{q \times \left[\frac{1}{H_O} + \frac{C_A S}{F_O \frac{m^3 - O_2}{m^3 - \text{gas}} \times 1300 \frac{\text{mg} - O_2}{m^3 - O_2}} \right]} \quad (3)$$

where H_O is the Henry's Law Constant for oxygen (about 30 (mg-O₂/m³-vapor)/(mg-O₂/m³-H₂O)). This expression assumes dissolution at the equilibrium concentration from the down-gradient edge of the oxygenated zone and use of oxygen for biodegradation at the up-gradient edge. For example, for the case where $L=3$ m, $q=0.1$ m/d, $F_O = 1$ m³-O₂/m³-gas (pure oxygen), and $C_A=10$ mg/L, then $\Delta T_O = 8$ d. For the same parameters,

except that $C_A = 1 \text{ mg/L}$ and 100 mg/L , the corresponding time estimates are $\Delta T_O = 13 \text{ d}$ and 2 d , respectively.

More specifics of gas delivery oxygenation systems are discussed below in §2.3

Step 6 – Preliminary Economic Analysis: Using reasonable assumptions about equipment needs, installation costs, and operating costs, a preliminary economic analysis is conducted. Information and the cost estimation spreadsheet tool presented in Miller et al. (2003b) can be used to conduct this analysis. It is recommended that this analysis consider a range of possible designs, ranging from a robust (over-designed) system to the actual projected design. The analysis can also be used to determine conditions (e.g., gas injection well spacings) that would make the technology impracticable.

Step 7 – Decision: - Is the System Design Necessary to Achieve the Technical Goals Economically Feasible? If the answer is “no”, then the performance expectations need to be changed, or a new technology is needed. If the answer is “yes”, then the user proceeds to Step 8.

Step 8 – Install, Operate, and Monitor the Oxygen Delivery System: The oxygen delivery system is installed and operated and changes in dissolved oxygen levels throughout the treatment zone are monitored with time. Periodic sampling of groundwater within the treatment zone every week or two weeks over the course of a month should be sufficient to gain a reasonable understanding of the performance of the oxygen delivery system.

Step 9 – Decision: - Are Dissolved Oxygen Levels in the Treatment Zone at, or Above, Target Concentrations ($>2 \text{ mg/L}$ and preferably $>4 \text{ mg/L}$)? If the answer is “no”, then the oxygen delivery system is modified to achieve the desired performance. This might involve the installation of additional wells, or the manipulation of operating conditions (injection pressures, durations, etc.). If the answer is “yes”, then the user proceeds to Step 10.

Step 10 – Decision: - Biostimulation vs. bioaugmentation? Bioaugmentation is clearly needed if MTBE degraders are not present in the aquifer. If microcosm tests or other evidence indicates the presence of MTBE degraders, then the increased oxygen levels might lead to sufficient degrading activity over time as the microbial population adjust to the new aerobic environment. Based on experience, the effect of biostimulation might not be observed for several months and the full effect might not be observed for a year. Therefore, it is important to determine if it is acceptable to wait and monitor the system performance over that time frame. It is also important to keep in mind that the impacts of bioaugmentation might not be clear for one to two months either.

If there is the need for more rapid response or monitoring data indicate inadequate performance resulting from biostimulation), then inoculation with MTBE degrading organisms will be necessary. Given their slow growth rate and low cell yields, it is recommended that high concentration culture be injected. For example, with the large-scale ESTCP biobarrier demonstration project at VCNB, cultures were injected with bacteria concentrations of about 2 mg-total suspended solids/L-solution.

Step 11 –Operate and Monitor System Performance: Groundwater samples are collected at agreed-upon frequencies and performance is assessed through review of concentrations of dissolved oxygen, MTBE, and other dissolved chemicals of interest. Monitoring wells should be placed up-gradient of the oxygenated zone, within the oxygenated/treatment zone, down-gradient of the well-oxygenated zone, and at the ends of the biobarrier. The latter are included to verify that the operation of the biobarrier does not cause a diversion of groundwater flow around the biobarrier.

2.3 THOUGHTS ON GAS INJECTION-BASED OXYGEN DELIVERY SYSTEMS

Figure 4 presents a simple schematic of the gas injection-based oxygen delivery system. The basic components are shown and these include gas delivery wells, an oxygen generator or air compressor, pressurized gas storage tanks, electronically-actuated solenoid valves, and a timer system. The basis for, and operation of this design are discussed briefly below.

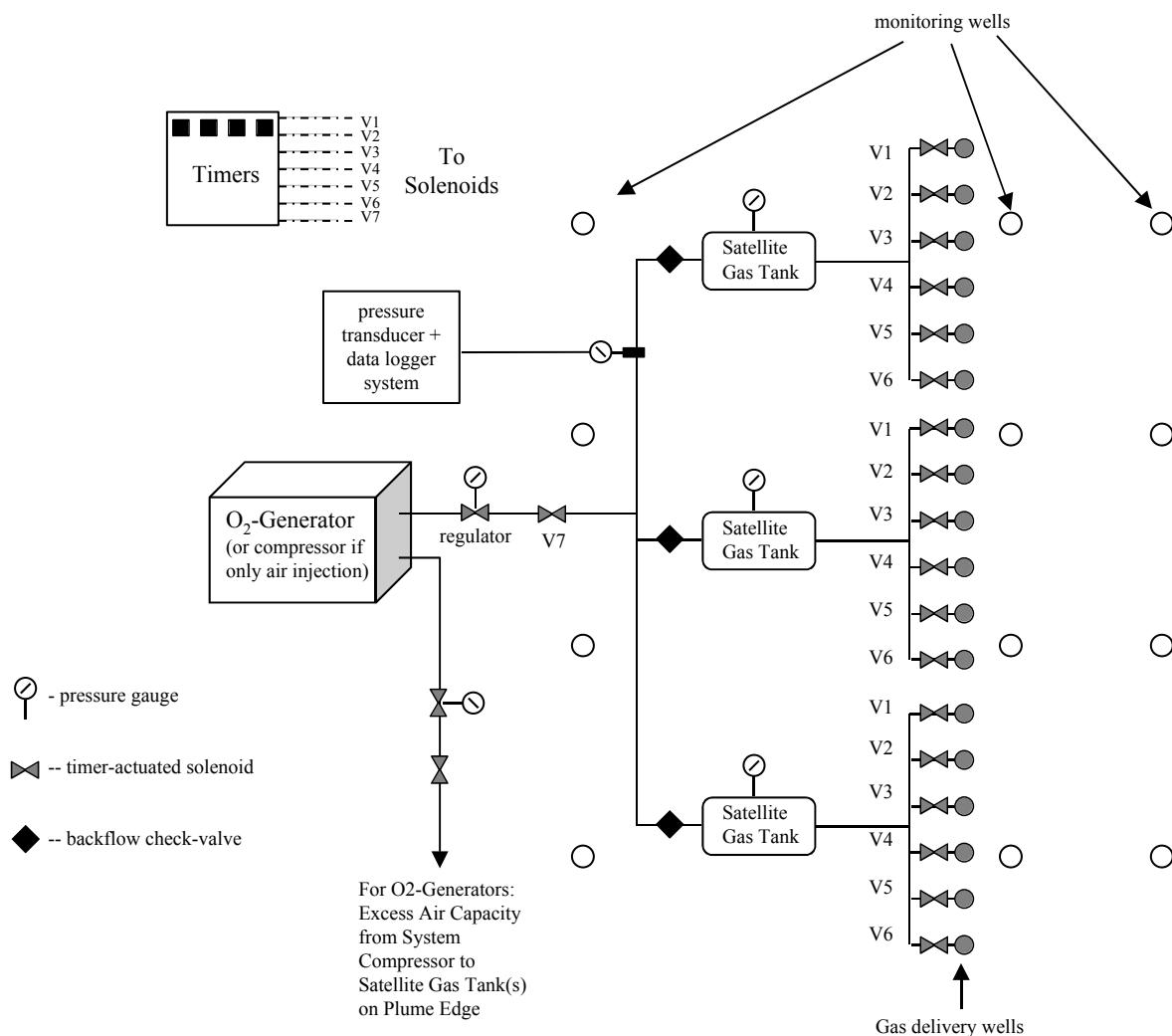


Figure 4. Schematic of a gas injection-based oxygen delivery system.

Pulsed Operation: To minimize the potential for the gas injection system to impact the groundwater flow direction, gas injection is periodic. As discussed above, the trapped gas remaining after each injection will continue to feed oxygen to the aquifer for a time period estimated roughly by Equation (3) given above in §2.2. In many cases, daily, or less frequent, gas injections will be sufficient. For example, for the ESTCP demonstration project at NBVC, gas was injected into each well four times a day.

High Intensity Injection of Short Duration: In general, broader gas distribution is achieved by higher intensity ($>10 \text{ ft}^3/\text{min}$) gas flows. Because the volume of gas required per well is generally not large, the flows can be of high intensity and of short duration. For example, for the ESTCP demonstration project at NBVC, wells were spaced approximately 1.2-m (4-ft) apart at two depths, and approximately 0.14 m^3 (5 ft^3) of gas was injected in about 0.5 min per well during each injection cycle.

Use of Oxygen Gas vs. Air: Arguably, both oxygen gas and air will provide oxygen to the subsurface, albeit at different concentrations. The pilot-scale and large-scale systems and VCNB utilized oxygen generators and oxygen gas injection, but both also contained sections of lower MTBE concentration where air was injected. Based on experience to date, air injection might be sufficient at lower concentrations sites ($<1 \text{ mg/L MTBE}$), but it is recommended that practitioners seriously consider oxygen gas injection for higher concentrations. The main reason is that gas distributions in aquifers are expected to be highly irregular and the higher equilibrium DO concentrations associated with oxygen, may help to compensate for these irregular and non-uniform gas distributions. Over the lifetime of a biobarrier project, the additional cost of an oxygen generator vs. an air compressor is not expected to be significant in most cases (Miller et al. 2003b).

Use of Satellite Pressurized Gas Storage Tanks and the Timer-Actuated Solenoid System: Commercially-available oxygen generators typically produce low flows ($<0.3 - 0.9 \text{ m}^3/\text{min}$, or $1 - 3 \text{ ft}^3/\text{min}$), but are capable of producing high pressures. Thus, satellite gas storage tanks are incorporated into the design in order to achieve the high intensity/short duration gas injection flows discussed above. For example, at VCNB, a $5 \text{ m}^3/\text{h}$ ($180 \text{ ft}^3/\text{h}$) oxygen generator was used to charge 15 0.07 m^3 (2.5 ft^3) gas storage tanks to a gauge pressure of about 3 atm (45 psig) (yielding about 0.3 standard m^3 , or 10 standard ft^3 of gas per tank). About 45 min was allowed for the pressurization cycle. This was then followed by injection of the gas stored in each satellite tank into a pair of wells connected to that tank (in about 30 s). Then the oxygen generator would recharge the tanks and gas would be injected into different pairs of wells, and this would continue until all wells had received a gas injection.

Gas storage tanks should be sized to provide the desired volume of gas to the aquifer for each injection. The minimum tank volume $V_{T,\min}$ [m^3] can be estimated:

$$V_{T,\min} = \frac{[L \times W \times D \times 0.3 \frac{\text{m}^3 - \text{pores}}{\text{m}^3 - \text{aquifer}} \times 0.05 \frac{\text{m}^3 - \text{gas}}{\text{m}^3 - \text{pores}}]}{N_{\text{wells}} \times (1 + \frac{P_{\text{tank}}}{P_{\text{Atm}}})} + V_{\text{pipe}} \times (1 + \frac{P_{\text{tank}}}{P_{\text{Atm}}}) \quad (4)$$

where L [m], W [m], and D [m] are the length, width, and depth of the target treatment zone, N_{wells} is the number of gas injection wells, P_{tank} [atm] is the gauge pressure of the fully-charged gas storage tank, P_{atm} is atmospheric pressure [1 atm], and V_{pipe} [m^3] is the volume of the piping between the solenoid valve and the top of the injection well screen. For example, for the large-scale demonstration system at VCNB $L=80$ m, $W=3$ m, $D = 3$ m, $N_{\text{wells}}=250$, $P_{\text{tank}} = 3$ atm, and $V_{\text{pipe}}=0.003 \text{ m}^3$. For these conditions, $V_{T,\min} = 0.023 \text{ m}^3 (=0.8 \text{ ft}^3)$. The actual tank size was 0.07 $\text{m}^3 (=2.5 \text{ ft}^3)$.

Other Benefits of the Gas Storage Tanks and the Timer-Actuated Solenoid System: The design shown in Figure 4 also helps to isolate gas injection wells from each other in order to maximize the gas distribution across all wells. Because the construction of each well is different, the common manifolding of a large numbers of gas wells is not recommended as it is very likely that most of the flow will go to one, or a few, of the wells (P.C. Johnson et al. (2001b)). If a few wells are to be connected to a common manifold, then it is necessary that the construction of those wells and the formations that they are installed in should be nearly identical.

Use of Modular Designs: The design shown in Figure 4 is modular, with the unit treatment cell consisting of a gas storage tank, six solenoid valves, and six wells. Replication of treatment cells helps to minimize the complexity of the project. For example, Figure 5 presents a photo of the unit treatment cell for the large demonstration system at NBVC. In this photo, all components are shown above-ground; however, one can visualize systems where all wells and associated piping are located in trenches and the satellite gas storage tanks and solenoid valves are located in nearby storage sheds.

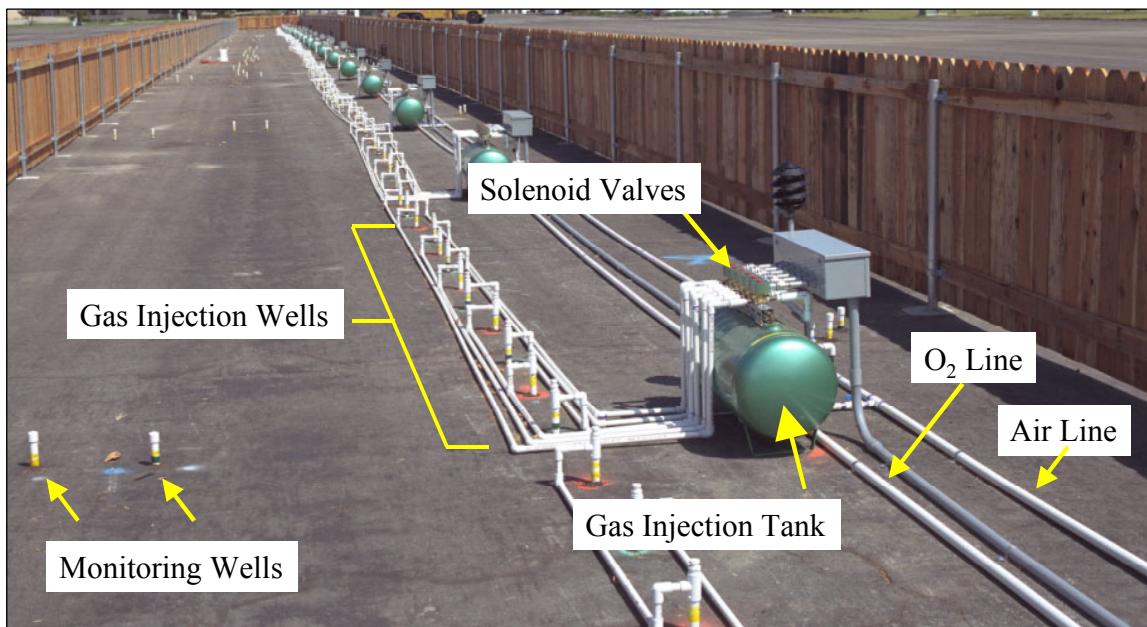


Figure 5. Picture showing the modular design of the large-scale demonstration system at VCNB (Miller et al. 2003a).

Sample Timer Sequence: Table 1 presents a sample timer sequence that is consistent with the modular design shown in Figure 4, for the case of one gas injection cycle per day. This same timer cycle could be used with larger biobarriers composed of any number of unit treatment cells.

Table 1. Sample timer sequence for a modular system where the unit treatment cells consist of a gas storage tank and six independent solenoid valves (consistent with Figure 4).

Time	Notes	V1 [normally closed]	V2 [normally closed]	V3 [normally closed]	V4 [normally closed]	V5 [normally closed]	V6 [normally closed]	V7 [normally open]
0:00	Begin Charging Tanks							
0:55	Discharge all tanks to well(s) connected to V1 valves	open	-	-	-	-	-	closed
1:00	Begin recharging tanks	closed	-	-	-	-	-	open
1:55	Discharge all tanks to well(s) connected to V2 valves	-	open	-	-	-	-	closed
2:00	Begin recharging tanks	-	closed	-	-	-	-	open
2:55	Discharge all tanks to well(s) connected to V3 valves	-	-	open	-	-	-	closed
3:00	Begin recharging tanks	-	-	closed	-	-	-	open
3:55	Discharge all tanks to well(s) connected to V4 valves	-	-	-	open	-	-	closed
4:00	Begin recharging tanks	-	-	-	closed	-	-	open
4:55	Discharge all tanks to well(s) connected to V5 valves	-	-	-	-	open	-	closed
5:00	Begin recharging tanks	-	-	-	-	closed	-	open
5:55	Discharge all tanks to well(s) connected to V6 valves	-	-	-	-	-	open	closed
6:00	End of Cycle	-	-	-	-	-	closed	open

Real-Time Process Monitoring of the Above-Ground System Components: Continuous-duty compressors and oxygen generators are fairly reliable when routine maintenance of the compressors is conducted. In addition, the other operating components of the oxygen delivery system (timer(s), solenoids, etc.) require little monitoring and maintenance. Thus, the system should be able to run for extended periods with minimal monitoring (visual inspection and verification of system operation every few days is generally sufficient). However, there are unplanned events (e.g., power failures, failed or sticking solenoids, etc.) that can render systems non-operational or compromise system performance. To minimize the amount of monitoring time and to validate above-ground system operation, it is recommended that practitioners conduct some real-time monitoring of the above-ground system operation. In particular, one easy option is to monitor the main gas manifold line pressure with a pressure transducer and data logger as shown in Figure 4. By reviewing the gas pressure vs. time history, one can tell if the system is likely to be charging and discharging properly as directed by the timer circuit.

2.4 THOUGHTS ON BIOAUGMENTATION INOCULATION METHODS

The pilot- and large-scale demonstrations of this technology have emphasized inoculation with relatively high concentrations of biomass, because MTBE-degrading organisms tend to be relatively slow growing and have low cell yields when grown on MTBE as a sole carbon source (Salanitro et al., 1994). It might be possible to introduce MTBE-degraders to the subsurface in more dilute solutions and then grow them to higher cell densities *in situ* on alternate carbon sources (e.g., Smith et al. 2003, Steffan et al. 1997, Okeke et al. 2003); however, it needs to be

recognized that bacteria from dilute solutions tend to be filtered out within a short distance of an injection well (e.g., Streger et al., 2002), and the non-native MTBE degraders have to compete with indigenous organisms for the alternate carbon source as it is introduced.

As stated above, this document focuses on the case where high density cell cultures are injected into the subsurface. For example, solutions having about 2.5 g-TSS/L (TSS = total suspended solids) were used for inoculation of the pilot- and large-scale demonstration systems, based on the specific activity of the culture (mg-MTBE degraded/g-TSS/d) obtained from microcosm tests and calculation of the MTBE flux to the biobarrier (groundwater specific discharge x MTBE concentration/ biobarrier cross-sectional area perpendicular to flow). These TSS concentrations are high enough to plug most conventional well screens, so delivery to the aquifer through conventional wells is not feasible. In addition, even if the well screens did not filter the suspended solids, the formation would filter the bacteria flocs over a short distance if the infiltration rate is slow (i.e., Streger et al., 2002).

In the work described by Miller et al. (2003a, b), inoculation was accomplished through the following approach:

- A Geoprobe rod with an expendable tip was pushed down to the deepest depth of the target treatment zone.
- The top of the rod was then connected to a 50 gal graduated container filled with MTBE-degrading culture through a hose, a high-pressure pump, and a series of valves. To prevent bacteria from settling, the solution was agitated by air sparging.
- The high pressure pump was turned on, and as the pressure increased in the rod, it was raised 6-inches. This caused the ejection of the expendable probe tip and the initiation of flow to the formation.
- Solution was injected at high pressures (often in excess of 30 psig) and at flows of about 5 gal/min).
- The drive rod was raised one foot for every 5 gal injected until the top of the treatment zone was reached. The rod was then removed and driven to depth again one foot laterally from the previous injection location.

For more insight to the use of this approach, the reader is referred to the two-dimensional lab-scale visualization studies conducted by Braunschneider (2000). There, the relationship between aquifer characteristics and bacteria distributions that result from this delivery method were examined. Bruanschneider's work includes photos of bacteria distributions with time during injection into a number of idealized geologies. In brief, that work shows that: a) distributions are roughly spherical and localized in coarse-grained sediments (sands and gravels), b) the injection causes fracturing and distribution of culture in the fractures for fine-grained soils (silts and clays), and c) the culture will travel through fractures in fine-grained soils to the more permeable layers in layered settings.

The mixed and single cultures used in the ESTCP-sponsored large-scale biobarrier demonstration (Miller et al., 2003a, b) were supplied by Shell Global Solutions, but these are no longer commercially available. A survey of vendors and consulting firms only found one vendor¹ that provided MTBE-degrading cultures with well-documented activity for use in bioaugmentation applications.

In cases where MTBE-degrading cultures are not commercially available or are too costly, it is possible to obtain MTBE-degrading organisms from sites where biodegradation is known to occur naturally, and then to grow sufficient quantities of the culture. Soil and/or groundwater from the site with known MTBE-degrading activity can be seeded into a properly-designed reactor (a high solids retention time is critical; Salanitro et al. 2004, Wilson et al. 2002, Zein et al. 2004) which is then fed with MTBE and nutrients. It should be noted, however, that it can take several months to grow sufficient quantities of MTBE-degrading organisms when beginning with soil and groundwater samples.

¹ - Envirogen, Princeton Research Center, 4100 Quakerbridge Road, Lawrenceville, NJ 08648-4702, Tel. (609) 936-9300, Fax (609) 936-9221

2.5 SAMPLE PERFORMANCE DATA

Miller et al. (2003a, b) provide details on the construction and costs associated with the large-scale ESTCP demonstration system at VCNB. Table 2 summarizes the key features of the site and biobarrier system.

Table 2. Summary of site and biobarrier system characteristics for the NBVC large-scale ESTCP demonstration project.

Site Characteristics	
Depth to groundwater and impacted aquifer thickness	Approximately 2.1 m (7 ft) below ground surface to groundwater, and the impacted saturated zone is about 4 m (13 ft thick)
Groundwater velocity	Approximately 0.3 m/d (1 ft/d) average linear velocity
Dissolved plume width and dissolved MTBE concentration	The dissolved plume is approximately 150 m (500 ft) wide with concentrations as great as 10 – 20 mg/L MTBE and 10 – 20 mg/L BTEX components.
Aquifer materials	The upper 1 m (3 ft) is composed of a silty/clayey fill material on top of 3 m (10 ft) of fine – medium sands.
System Characteristics	
Gas injection wells	Deep and shallow gas injection wells having 0.5 m (1 - 2 ft) screens were installed at 6 m (20 ft) and 4.5 m (15 ft) depths. The wells were spaced 0.6 m (2 ft) apart in an alternating deep-shallow sequence.
Gas delivery	The highest MTBE concentration regions received oxygen gas, while other portions received air injection. The oxygen gas was supplied by an oxygen generator system and the air was supplied by the excess compressor capacity of the oxygen generator system.
Unit treatment cell	Each unit treatment cell was comprised of 12 wells (6 deep and 6 shallow wells). Pairs of deep or shallow wells were connected to a manifold having six solenoid valves, and the manifold was connected to a 0.07 m^3 (2.5 ft ³) gas storage tank. For each injection cycle the storage tank was pressurized to a gauge pressure of 3 atm (45 psig). Four injection cycles were completed each day.
Timer sequence	The sequence was very similar to that presented in Table 1, with that sequence being repeated every 6 h (4 times daily)

Figure 6 presents a plan view of the well-layout showing the locations of gas injection and monitoring wells.

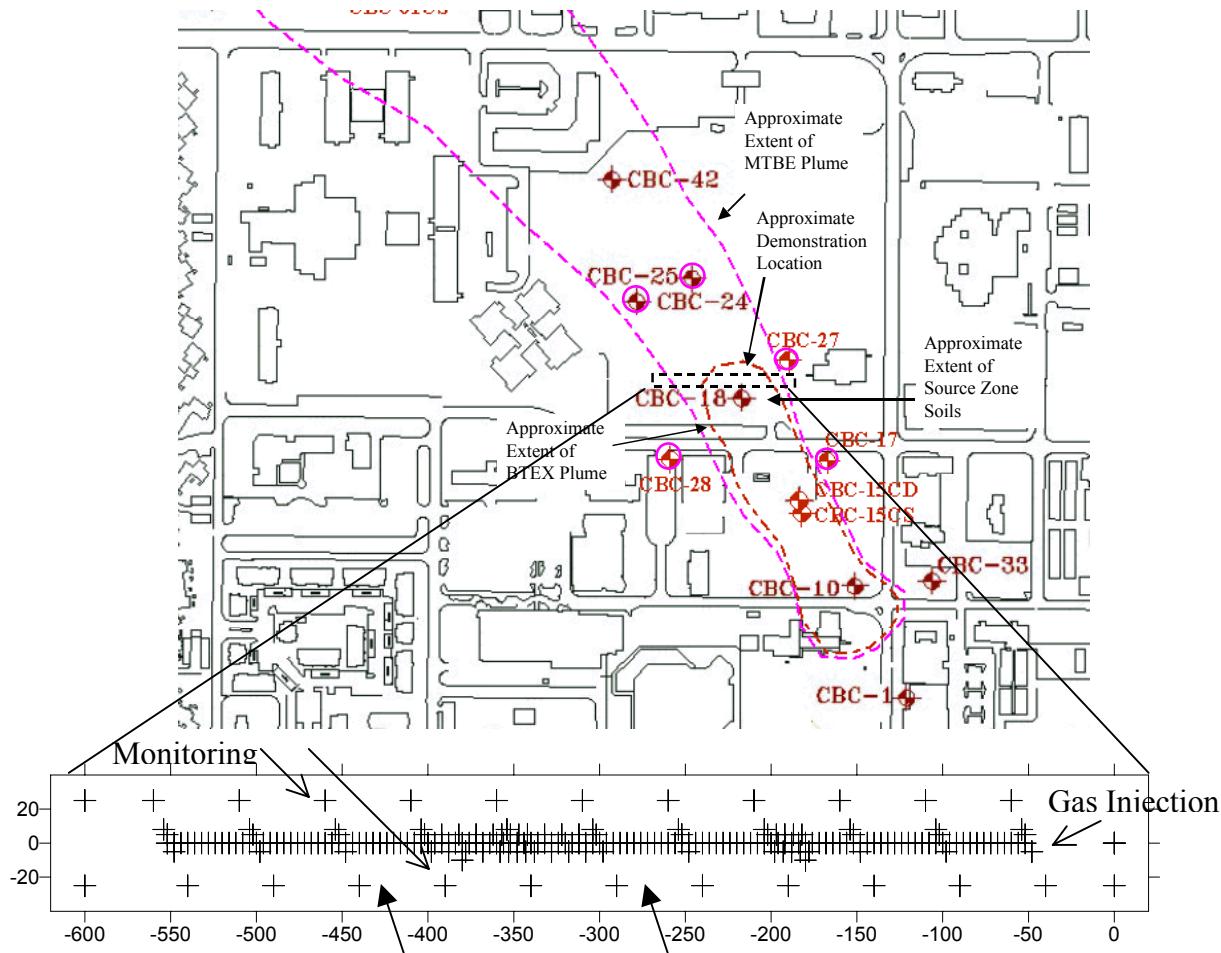


Figure 6. Plan view map showing approximate locations of the MTBE plume, BTEX plume, demonstration site location, and locations of monitoring and gas injection wells. Groundwater flows in the direction of the two arrows below the figure. The lateral dimensions are shown in ft from the northernmost well (at the right), and the vertical dimensions are also in ft measured from the gas injection wells row.

Performance data are presented as a series of snapshots in time in Figure 7 (dissolved oxygen) and Figure 8 (dissolved MTBE). Each contour plot represents over 225 data points (76 up-gradient, 94 down-gradient, 55 along the line of gas injection and inoculation points). The first two contours show the state of the system before the gas injection system was turned on, the third contour shows the site conditions at the time of the bioaugmentation, the last four contours show concentration distributions at 1, 3, 10, and 15 months after bioaugmentation.

CHAPTER 3. CONCLUDING REMARKS

This document presents a paradigm for the design, monitoring, and optimization of in situ methyl tert-butyl ether (MTBE) aerobic biobarriers. This design paradigm is based on experience gained while designing, monitoring, and optimizing pilot-scale and full-scale MTBE biobarrier systems – most notably, the systems studied at the Naval Base Ventura County (NBVC) at Port

Hueneme, CA. As it is based on limited experience to date, the paradigm should be reviewed and revised (as necessary) as more experience is gained with this technology.

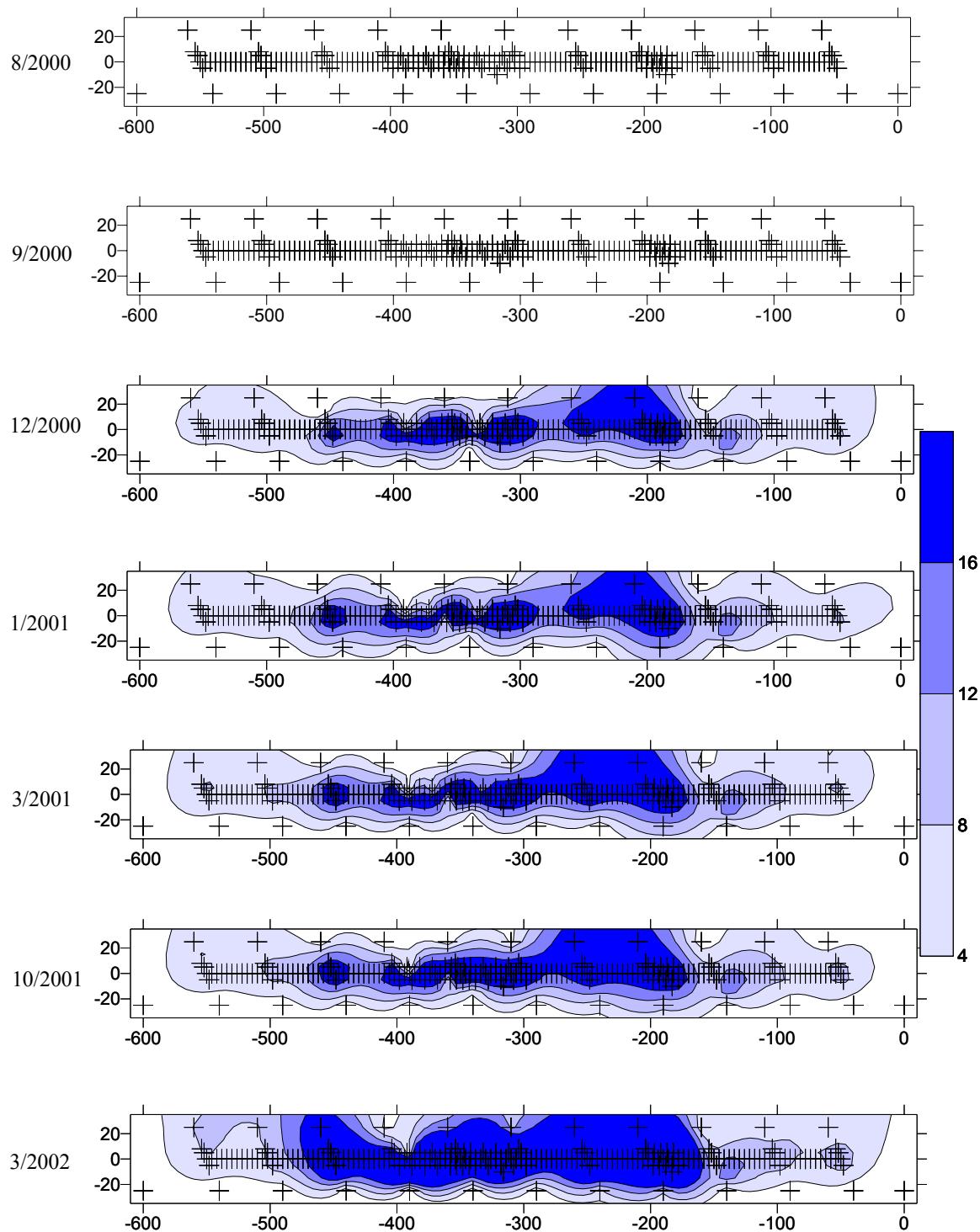


Figure 7. Dissolved oxygen time-series data (in mg-oxygen/L-groundwater); each “+” represents paired shallow and deep wells. Groundwater flows approximately from the bottom to the top of each figure.

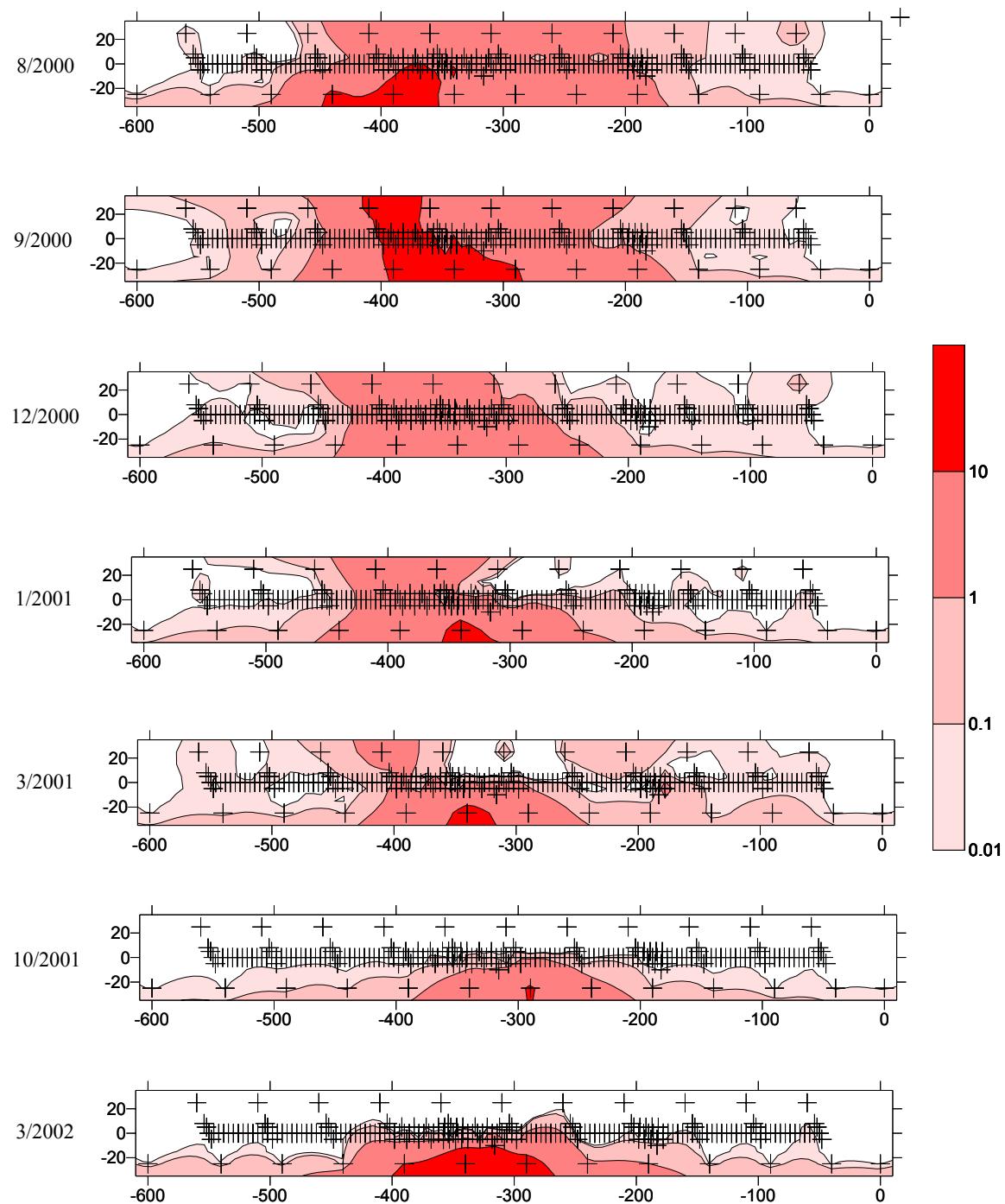


Figure 8. MTBE concentration time-series data (in mg-MTBE/L-groundwater); each “+” represents paired shallow and deep wells. Groundwater flows approximately from the bottom to the top of each figure. Lateral dimensions are shown in feet from the northernmost well, and the vertical dimensions are also in feet measured relative to the position of the row of gas injection wells.

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